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(71)Applicant : INST FR PETROLE
(72)Inventor : BENAZZI ERIC
HIRSCHAUER ANDRE
JOLY JEAN-FRANCOIS
OLIVIER HELENE
BERNHARD JEAN-YVES

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(54) CATALYST FOR ALKYLATION OF PARAFFIN

(57)Abstract:

PURPOSE: To manufacture a paraffin compound having a high degree of net structure and high octane number.

CONSTITUTION: This catalyst is a catalyst for alkylation of paraffin comprising at least one kind of mixture composed of an organic or inorganic porous support having a relative surface area of 0.01-1500 m²/g, total pore volume 0.005-1.5 cm³/g, and at least one kind of halogenide of aluminium and/or boron, and at least one kind of halohydroamine and/or halogenated ammonium. This catalyst is used for contact alkylation reaction of isobutane and/or isopentane in the presence of at least one kind of olefin having 2-6 carbon atoms per one molecule.

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CLAIMS

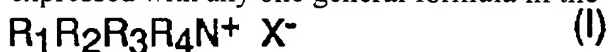
[Claim(s)]

[Claim 1] specific surface area of 0.01-1500m² / g -- the total -- with at least one sort of halogenides of the compound chosen from the group which consists of organic or inorganic porosity support, and the aluminum and boron of pore volume 0.005 -1.5 cm³/g ammonium halide and halo hydration amine (halohydrate d'amine) from -- catalyst for alkylation of paraffin into which it is a catalyst containing the mixture which consists of at least one sort of compounds chosen from the becoming group, and this support sinks with said mixture.

[Claim 2] The catalyst by claim 1 which is the ion complex with which said mixture does not mix with the hydrocarbon phase which is a liquid at the time of sinking in to support.

[Claim 3] the halogenide of the compound chosen from the group which consists of aluminum and boron -- AlCl₃ and AlBr₃ And AlF₃ from -- catalyst by claims 1 or 2 chosen from the becoming group.

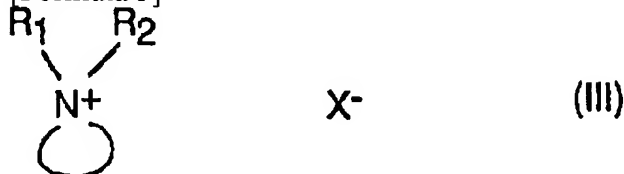
[Claim 4] The catalyst by one of claims 1-3 said whose compounds are the fourth ammonium of halogenation expressed with any one general formula in the following general formula: [Formula 1]



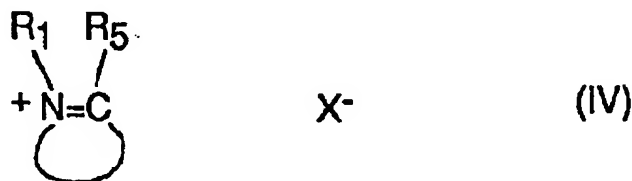
[Formula 2]



[Formula 3]



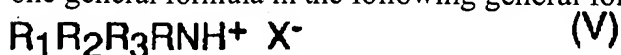
[Formula 4]



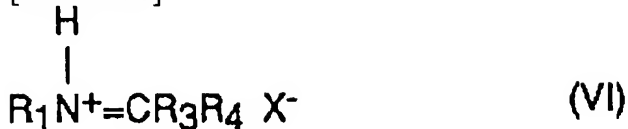
(R₁, R₂, R₃, R₄, or R₅ expresses hydrocarbon (hydrocarbyle) residue among a formula, further, R₅ may be hydrogen and X⁻ expresses halogenide ion).

[Claim 5] The catalyst by one of claims 1-4 said whose compounds are the chloride of N and N' dialkyl imidazolium, a bromide, the chloride of N-alkyl pyridinium, or a bromide.

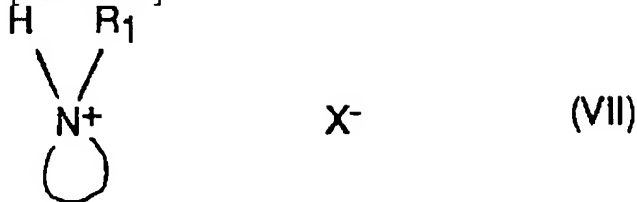
[Claim 6] The catalyst by one of claims 1-3 said whose compounds are the halo hydration amines expressed with any one general formula in the following general formula: [Formula 5]



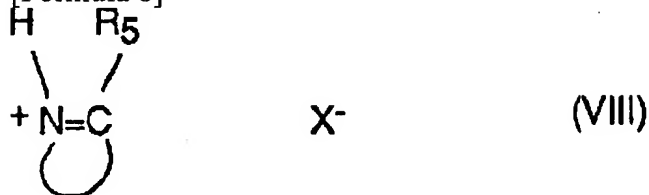
[Formula 6]



[Formula 7]



[Formula 8]



(the inside of a formula, R1, R2, R3, R4, or R5 is the same -- or it differs, hydrocarbon (hydrocarbyle) residue or hydrogen is expressed, and X- expresses halogenide ion) .

[Claim 7] Said compound is pyridinium salt (chlorhydrate), for example, the chloro hydrate of pyridinium. And a BUROMO hydrate (bromhydrate), The chloro hydrate of 2-pico RINIUMU and a BUROMO hydrate, the chloro hydrate of 3-pico RINIUMU, and a BUROMO hydrate, The chloro hydrate of 4-pico RINIUMU and a BUROMO hydrate, the chloro hydrate of piperidinium, and a BUROMO hydrate, The chloro hydrate of PIPERAJINIUMU and a BUROMO hydrate, the chloro hydrate of mol HORINIUMU, and a BUROMO hydrate, The catalyst by one of claims 1, 2, 3, or 6 which are the halo hydration amines chosen from the group which consists of the chloro hydrate of methyl-2-pyrazinium, a BUROMO hydrate, a chloro hydrate of pyrrolidinium, and a BUROMO hydrate.

[Claim 8] The manufacture approach of the catalyst by one of claims 1-7 into which support is calcinated and it subsequently sinks with said mixture.

[Claim 9] How to use the catalyst by one of claims 1-7, or the catalyst manufactured by claim 8 in the contact alkylation approach of at least one sort of components chosen from the group which consists of the isobutane and isopentane by at least one sort of components chosen from the group which consists of an olefin which has 2-6 carbon atoms per molecule.

[Claim 10] Operation by claim 9 whose reaction temperature is 5 degrees C or less.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention Organic or inorganic porosity support and aluminum, and/or at least one sort of halogenides of boron, The catalyst containing at least one sort of mixture which consists of the fourth ammonium of halogenation, and/or halo hydration amines, And at least one sort of olefins which have 2-6 carbon atoms per molecule, Namely, C2 - C6 It is use of this catalyst in the contact alkylation approach of of the isobutane and/or isopentane using an olefin, and is related with the use which can manufacture whenever [high reticulated-ized], and the paraffin series compound which has a high octane value.

[0002]

[Description of the Prior Art] Control point fire (allumage commande) In order to supply an internal combustion engine and the engine of especially high compressibility, it has a high octane value, namely, it is known that especially the thing using the evaporation fuel which consists of paraffin hydrocarbon mainly strongly made reticulated is advantageous. Such matter can be obtained according to the alkylation of isoparaffin (an isobutane and/or isopentane) by the olefin which has 2-6 carbon atoms per molecule. Extract of the hydrate of an olefin which especially produces the low, a parasitism reaction, for example, an octane value, hydrocarbon and the unsaturated hydrocarbon which are hardly made reticulated (abstraction) It is necessary to use a very acidity catalyst for this reaction a case to reduce a reaction and a polymerization reaction, a decomposition reaction, and disproportionation.

[0003] C2 - C6 A sulfuric acid or a hydrofluoric acid is used for the industrial approach which is existing about manufacture of the hydrocarbon by alkylation of the isobutane by the olefin, and/or an isopentane as a catalyst. In these approaches, an acid catalyst makes the liquid phase. In order to make an emulsion, this is contacted into isoparaffin (kind)-olefin (kind) liquid mixture. These approaches have high cost and a big problem is produced to an environment as opposed to human being's insurance. In order to solve these problems, a different catalyst system from the sulfuric acid of the liquid phase and a hydrofluoric acid was studied.

[0004] In order to carry out the catalyst of the alkylation reaction of the isoparaffin by the olefin, development of the acid catalyst from many acid solid-states of various classes is already proposed. The following are mentioned as a thing of the group of an acid catalyst. Namely, molecular sieving (for example, US-A -3,236,762, US-A -3,251,902, US-A -3,644,565, US-A -4,377,721, US-A -4,384,161, and US-A-4,300,015 reference), Depending on the case, he is BF₃. Macro reticulated-ized resin put together (for example, US-A -3,855,342, US-A -3,855,343, US-A -3,862,258, and US-A-3,879,489 reference), NAFION mold perfluoro-resin (resine perfluoree) (for example, US-A -4,056,578 and US-A-4,038,213 reference), Lewis acid and/or Broensted acid (for example, US-A-3,975,299, US-A-3,852,371, and US-A-3,979,476 reference) which were supported on various inorganic support, A chlorination alumina (for example, US-A -3,240,840, US-A -3,523,142, US-A -3,607,859, US-A -3,523,142, US-A -4,066,716, US-A -4,083,800, and US-A-4,066,716 reference), The graphite in which Lewis acid and/or Broensted acid were inserted (for example, US-A -4,083,885, US-A -4,116,880, US-A -4,128,596, and US-A-3,976,714 reference), And an oxide 4, for example, ZrO₂ / SO, It is the anion (for example, J-01288329, J-011245854-A, J-01245953, J-61242641-A, and J-61242641 reference) supported on support. Although led to manufacture of reticulated-ized isoparaffin from these solid-states, this has some big faults. In order to restrict the magnitude of second order reaction, and the lowness (inhibition of the catalyst by the sediment of partial saturation oligomer) of the stability of catalytic activity with time as a fault, in many cases, use of a very high isoparaffin (kind)-olefin (kind) mole ratio can be mentioned. Therefore, these catalysts must be reproduced

frequently. Furthermore, high reaction temperature must be used by the lowness of some of some acid solid-states, for example, the acidity of molecular sieving. This is harmful to manufacture of the hydrocarbon of a high octane value.

[0005]

[Means for Solving the Problem] This invention relates to the new catalyst which can obtain the paraffin series compound which has whenever [isobutane and/or isopentane, and high reticulated according to alkylation of isobutane preferably-ized], and, a high octane value using at least one sort of olefins which have 2-6 carbon atoms per molecule.

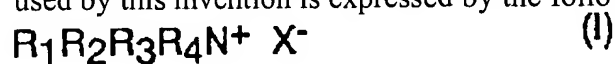
[0006] At least one sort of halogenides of the compound chosen from the group which the catalyst of this invention becomes from organic or inorganic porosity support, and boron and aluminum, namely, aluminum and/or at least one sort of halogenides of boron -- with aluminum halide preferably At least one sort of compounds chosen from the group which consists of ammonium halide and a halo hydration amine, That is, at least one sort of ammonium halides and/or a halo hydration amine, and the mixture that consists of at least one sort of ammonium halides, a chloro hydration amine, and/or a BUROMO hydration amine preferably are included. It sinks in with at least one sort of mixture with which this support consists of aluminum and/or at least one sort of halogenides of boron, and at least one sort of ammonium halides and/or a halo hydration amine. Said mixture is an ion complex which does not usually mix with the hydrocarbon phase called "fused salt." although this can be obtained with a liquid with ambient temperature -- the same -- higher temperature -- it can obtain below by 100 ** still more preferably below 150 ** preferably. In any case, this is a liquid in the case of sinking [of this to support] in.

[0007] Support is chosen from organic [which was known by this contractor] or inorganic porosity support. As organic support which can be used, macro reticulated resin, perfluoro-resin, and carbon can be mentioned as an example of un-limiting-. As inorganic support which can be used, an oxide 2, for example, SiO, ZrO₂, TiO₂, SnO₂, aluminum 2O₃, Fe 2O₃, HfO₂, and all at least two combination (for example, ZrO₂-TiO₂) of these compounds can be mentioned. Desirable support is a silica.

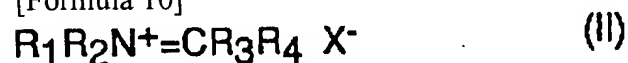
[0008] the specific surface area of the support which can be used -- general -- 0.01-1500m² / g -- desirable -- 0.01 - 150 m² / g -- they must be 0.01-50m² / g still more preferably. the total pore volume of support -- general -- 0.005 - 1.5 cm³ / g -- desirable -- 0.005-1cm³ / g -- they must be 0.005 - 0.8 cm³ / g still more preferably. Generally one sort or said two or more mixture must occupy the part of 5 - 100 % of the total pore volume of oxide support in the case of sinking [of said support by at least one sort of mixture which consists of aluminum and/or at least one sort of halogenides of boron, and at least one sort of ammonium halides and/or halo hydration amines] in. thus, the acquired catalyst -- general -- 0.01 - 500 m² / g -- desirable -- 0.01 - 150 m² / g -- it is characterized by the specific surface area of 0.01-40m² / g still more preferably.

[0009] the halogenide of the aluminum which can be used in this invention in more detail, and/or boron -- aluminum and/or the 3 fluorides of boron, trichloride and/or a tribromide 3, for example, AlCl₃, AlBr₃, BCl₃, or BBr₃ -- desirable -- the 3 fluorides of aluminum, trichloride and/or a tribromide 3, for example, AlCl₃, AlBr₃, and AlF₃ it is . One side of a halogenide can use these at a rate to 99% with various another side from 99% as a pure substance or mixture. Therefore, AlCl₃ AlBr₃ and AlCl₃ BCl₃ or AlBr₃ BBr₃ You may mix.

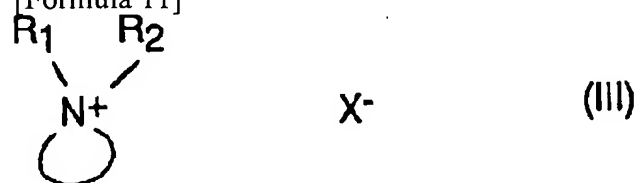
[0010] : to which the fourth ammonium of halogenation which makes a part of non-ring type or ring, and which can be used by this invention is expressed by the following general formula in more detail -- [Formula 9]



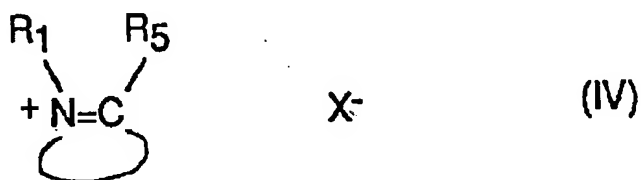
[Formula 10]



[Formula 11]



[Formula 12]



[0011] the inside of a formula, R1, R2, R3, R4, or R5 the same -- or -- differing -- hydrocarbon (hydrocarbyle) residue, for example, alkyl, cycloalkyl, aryl, an aralkyl, or alkyl aryl -- expressing -- R5 Hydrogen or hydrogen, and carbon may be the permutation hydrocarbon residue containing at least one different atom, for example, nitrogen, again.

Furthermore, one radical may be able to set to one two molecules which are the things of these which has above at least one. R1 R2 N+=CR3-R6-CR3 =N+R1 R2 2 [for example,] (X-) it is . R6 one radical -- it is -- further -- alkylene residue -- or you may be phenylene residue again. formula (III) (IV) a ring -- 4-19 atoms -- it may consist of 5-6 atoms preferably, and other nitrogen atoms may be included out of the nitrogen of the fourth ammonium depending on the carbon atom or the case. These rings may be aromatic series or may not be aromatic series. formula (III) and condensation of the ring of (IV) is carried out with other rings -- you may have -- R1 ***** -- although it defined, you may have a hydrocarbon substituent [like], an amine functional group, a fluorine, chlorine, or a bromine atom.

[0012] A radical R1, R2, R3, R4, and R5 It can carry out and methyl, ethyl, propyl, isopropyl, butyl, the second butyl, tertiary butyl, amyl, methylene, ethylidene, phenyl, or benzyl can be mentioned. R6 You may be methylene, ethylene, a propylene, or a phenylene group. The main things of the ring indicated by the formula (IV) belong to the group of a pyridine, an imidazole, triazine, a pyrazole, a pyrimidine, and triazole.

[0013] These formulas (I) It sets to - (IV) and is X. - Halogenide ion, for example, bromide ion, or chloride ion is expressed.

[0014] As an example of the ammonium salt which can be used by this invention, in more detail The chloride and bromide of imidazolium and salt of pyridinium, for example, N, and N'-dihydrocull BIRUIMIDAZORIUMU, and N-hydrocarbyle pyridinium, Especially The chloride of 1-methyl-3-ethyl imidazolium, the bromide of 1-methyl-3-butyl imidazolium, The chloride of 1-phenyl-3-isopropyl imidazolium, the chloride of N-methyl pyridinium, the bromide of N-isopropyl pyridinium, and the chloride of N-benzyl pyridinium can be mentioned.

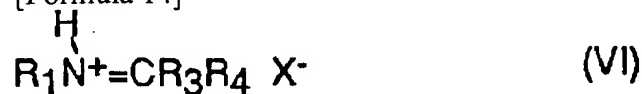
[0015] In more detail, although the halo hydration amine which can be used by this invention contains one mol [per one mol of amines] halo hydro acid, even if there are per one mol of amines similarly, it may contain two-mol halo hydro acid, and contains two mols [per one mol of amines] halo hydro acid preferably. [few] Moreover, the halo hydrate mixture containing the halo hydrate mixture containing at least one-mol halo hydro acid, 1 [for example,], and two-mol halo hydro acid can also be used.

[0016] : corresponding to [said halo hydration amine originates in an amine, ring type diamine, or the amine that makes a part of ring which may have at least one nitrogen atom, and] the following general formula in these --

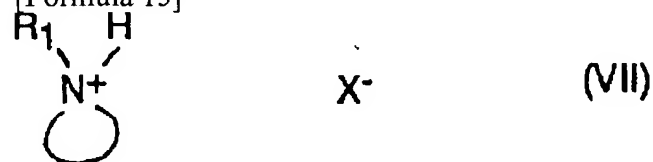
[Formula 13]



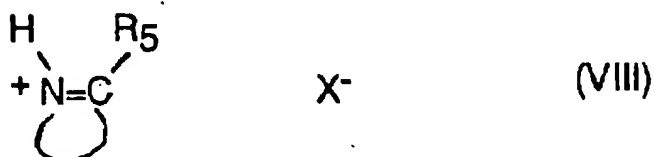
[Formula 14]



[Formula 15]



[Formula 16]



[0017] the inside of a formula, R1, R2, R3, R4, or R5 the same -- or -- differing -- hydrocarbon residue, for example, alkyl, cycloalkyl, aryl, an aralkyl, or alkyl aryl -- expressing -- or -- further -- hydrogen -- expressing -- R5 Hydrogen and carbon may be the permutation hydrocarbon residue containing at least one sort of different atoms, for example, nitrogen, again. In order to obtain a halo hydration amine, one radical may also be able to set to one further two molecules which are the things of these which has above at least one. R1 $\text{HN}=\text{CR}_3\text{-R}_6\text{-CR}_3=\text{N}+\text{R}_1$ R2 2 (X-) or R1 $\text{HN}=\text{CR}_3\text{-R}_6\text{-CR}_3=\text{N}+\text{R}_1$ H(X-) 2 it is . [for example,] R6 one radical -- it is -- alkylene residue -- or you may be phenylene residue again. formula (VII) (VIII) a ring -- 4-19 atoms -- it may consist of 5-6 atoms preferably, and the other nitrogen atoms other than the nitrogen of an amine may be included depending on the carbon atom or the case. These rings may be aromatic series or may not be aromatic series. formula (VII) and (VIII) carries out condensation of the ring with other rings -- you may have -- R1 ***** -- although it defined, you may have a hydrocarbon substituent [like], an amine functional group, a fluorine, chlorine, or a bromine atom.

[0018] A radical R1, R2, R3, R4, and R5 It can carry out and a hydrogen atom, methyl, ethyl, propyl, isopropyl, butyl, the second butyl, tertiary butyl, amyl, methylene, ethylidene, phenyl, or benzyl can be mentioned. R6 You may be methylene, ethylene, a propylene, or a phenylene group. The main things of the ring indicated by the formula (VIII) belong to the group of a pyridine, an imidazole, triazine, a pyrazole, a pyrimidine, and triazole.

[0019] these formulas (V) - (VIII) -- setting -- X- halogenide ion -- bromide ion or chloride ion is expressed preferably.

[0020] As an example of the chloro hydration which can be used by this invention, and a BUROMO hydration amine, the chloro hydrate and BUROMO hydrate of the chloro hydrate of the salt of pyridinium, for example, the chloro hydrate of pyridinium, a BUROMO hydrate, 2-pico RINIUMU, 3-pico RINIUMU, or 4-pico RINIUMU and a BUROMO hydrate, piperidinium, PIPERAJINIUMU, mol HORINIUMU, methyl-2 and pyrazinium, and pyrrolidinium can be mentioned in more detail.

[0021] In the case of the fixed component of a class, the relative rate of the halogenide of aluminum and/or boron, and an ammonium halide (kind) and/or a halo hydration amine (kind) determines the acidity (or basicity) of this medium, and the crystallization point of this as coincidence. The mole fraction of the halogenide (kind) of aluminum and/or boron is 0.5. When it is the following, mixture is seldom acidity but basicity further. A mole fraction is 0.5. If it is above, a medium will become acidity higher as this mol fraction is large. Therefore, the range variously changeable according to the reactivity of an olefin of very wide range acidity can be used. This has the advantage of making a reaction rate into max and making a parasitism oligomerization reaction into the minimum.

[0022] The manufacture approach of the catalyst by this invention includes two processes. Generally in the first process, 50 degrees C or more of 80 degrees C or more of support are preferably calcinated still more preferably at the temperature of 200 - 600 **, for example, about 500 **. The time amount of this baking process is usually 10 minutes - 50 hours. Carrying out baking under existence of air or air / nitrogen mixture, generally a flow rate is 0.001 - 10 l/h/g. The second process is sinking [which consists of aluminum and/or at least one sort of halogenides of boron, and at least one sort of ammonium halides and/or a halo hydration amine / of the product calcinated with at least one sort of mixture] in. As for sinking-in temperature, one sort or said two or more mixture seem to be a liquid in the case of sinking [of support] in. In order to carry out this process, all the techniques well known to this contractor can be used. Next, the solid-state obtained by doing in this way avoids humidity, and is saved. The catalyst by this invention consists of organic [into which it sank with at least one sort of mixture] or the inorganic porosity support which follows and consists of aluminum and/or at least one sort of halogenides of boron, and at least one sort of ammonium halides and/or a halo hydration amine.

[0023] Even if the catalyst by this invention is used as a pure substance, it may be diluted and used by the various matter in which catalytic activity is seldom shown in this reaction. These matter is a silica, an alumina, a magnesia or further various clay, for example, a bentonite, a montmorillonite, or a kaolin.

[0024] It is used in the approach by which an olefin and/or olefin mixture are the liquid phase, and said catalyst is advantageously introduced into a reactor as isoparaffin mixture as mixture with isoparaffin. A catalyst may be used as

suspension in the liquid phase of the reagent given to still more efficient stirring as the fixed bed, the moving bed, or the fluid bed.

[0025] per hour when isoparaffin (kind)-olefin (kind) mixture was displayed by the weight of the olefin introduced per gravitational unit of a catalyst per hour -- space velocity -- general -- $0.001 - 10h^{-1}$ -- it may be preferably introduced into a reactor by $0.002 - 2h^{-1}$. Said mixing may be carried out inside a reactor again. In the case of which, the mixture constituted in this way has hydrocarbon mixture within a reactor under a pressure which is still a liquid on a catalyst, and a temperature condition.

[0026] Although reaction temperature is generally $-50^{\circ}C - 150^{\circ}C$, when reaction temperature is $-5^{\circ}C$ or less still more preferably, as for catalyst results, it is improved $0^{\circ}C$ or less preferably $5^{\circ}C$ or less. the pressure of a reactor -- temperature -- what kind of thing -- be -- it must be enough within a reactor to maintain a hydrocarbon in the liquid condition.

[0027] In order to restrict second order reaction, generally superfluous isoparaffin (kind) is used to one sort or two or more olefins. For example, in alkylation of the isobutane by the butene, an isobutane is introduced with the gestalt of the butane mixture containing at least 40% of isobutane, while it has been pure in a brewing raw material. Furthermore, isomer butene mixture may be introduced into a pure butene or a paraffin. any case -- the isobutane / butene (kind) mole ratio in a brewing raw material -- general -- $1-100$ -- it is $5-10$ preferably [it is desirable and / in the case of $3-50$, and many].

[0028] A resultant is France specification-.M.07.071 in March, 1969. It is regularly controllable by measurement of the bromine number by the project.

[0029] If the class of catalyst and the operating condition (especially temperature) of a catalyst are chosen appropriately, manufacture of the alkylation product of the paraffin (kind) by at least one sort of olefins will be attained according to the catalyst by this invention. These products are advantageous as a component of the evaporation fuel for engines, and a gasoline, and these contain the compound which has not been saturated with 60(mol) % at least in the paraffin which has eight carbon atoms per molecule below 1(mol) %. The paraffin which has eight carbon atoms per molecule consists of a trimethyl pentane of $70 - 98(mol) \%$.

[0030] Another advantage of the catalyst by this invention is the olefin mixture which has 2-6 carbon atoms per molecule, and is being able to alkylate an isobutane at low temperature. In this mixture, the rate of an olefin of having five carbon atoms even if few per molecule is very large (at least 10 % of the weight, preferably at least 40 % of the weight).

[0031]

[Example] The range is not restricted although the following example illustrates this invention.

[0032] [Example 1]

manufacture of a catalyst -- : which manufactures an ion complex with a normality of 0.55 Ns as follows -- newly sublimated 10.3g $AlCl_3$ 10.9g methylbutyl imidazolium chloride is added slowly, stirring with a magnetic stirring rod. Temperature is uniformly maintained at $0^{\circ}C$. Thus, the mixture of a liquid is obtained with a mere ambient temperature colored for a while. This salt avoids moisture and is saved.

[0033] Macropore silica 14g of the specific surface area of $27m^2 / g$ is activated by baking by $500^{\circ}C$ for bottom 4 hours of air. Thus, the activated solid-state is saved under an argon. Next, it performs desiccation sinking [of 10g of solid-states calcinated by mixture 4.5 g prepared as mentioned above] in. Thus, the acquired catalyst contains mixture 4.5 g and silica 10g, and this is saved under an argon at $-18^{\circ}C$.

[0034] 12g of catalysts manufactured according to said approach is introduced into Fischer [of volume 360 ml beforehand purged by alkylation argon flowing down of the isobutane by 2-butene] -, and the glass reactor of - porter mold. Subsequently, close [of a catalyst] closes the reactor which is, and then makes it primary reduced pressure, and, subsequently it cools it at $-20^{\circ}C$.

[0035] Subsequently, isobutane 72cm³ It adds to the reactor containing a catalyst under stirring. Said reactor is sunk into a $-20^{\circ}C$ cold bath. In order to make temperature into homogeneity, a catalyst system + isobutane is left under stirring for 30 minutes.

[0036] They are 6 hours and 13.16 cm³ at all. 2-butene is added regularly and the temperature of a reactor is maintained at $-15^{\circ}C$ all the time between impregnation time amount.

[0037] A hydrocarbon phase is extracted from a reactor after a reaction, and an isobutane is evaporated slowly. Alkylation objects are collected and this is analyzed by the vapor phase chromatography. The weight composition of

this is shown below. The conversion ratio of an olefin is 100 %. The presentation of an alkylation object is summarized in the following table 1.

[0038]

[Table 1]

1 C ₅	1. 0
C ₆	0. 9
C ₇	1. 6
C ₈	93. 8
C ₉	1. 2
C ₉₊	1. 5

[0039] C₈ The research octane number according [a fraction] to count including 94.6% of the weight of a trimethyl pentane is 99.

[0040] The contact alkylation test of the isobutane by 2-butene is repeated using the same catalyst as the [example 2] example 1. A series of tests at various temperature are carried out. A result is summarized in the following table 2.

[0041]

[Table 2]

T (°C)	C ₅ - C ₇	C ₈	C ₉₊	RON
- 20	2. 8	92. 3	4. 9	99. 3
- 10	2. 1	97	0. 9	98. 4
0	6. 4	86. 7	6. 9	96. 4

[0042] This table clarifies the advantage in the case of operating it at low temperature.

[0043] [Example 3]

manufacture of a catalyst -- : which manufactures an ion complex with a normality of 0.67 Ns as follows -- newly sublimated 24.8g AlCl₃ 11.5g chloro hydration pyridinium (chlorhydrate de pyridinium) is added slowly, stirring with a magnetic stirring rod to the suspension in a heptane. Thus, the mixture of a liquid is obtained with a mere ambient temperature colored for a while. This mixture avoids moisture and is saved under an argon.

[0044] Macropore silica 13g of the specific surface area of 27m² / g is activated by baking by 500 ** for bottom 4 hours of air. Thus, the activated solid-state is saved under an argon. Next, it performs desiccation sinking [of 13g of solid-states calcinated by mixture 8.8 g prepared as mentioned above] in. Thus, the acquired catalyst contains mixture 8.8 g and silica 13g, and this is saved under an argon at -18 degrees C.

[0045] The catalyst manufactured according to said approach is introduced into Fischer [of volume 360 ml beforehand purged by alkylation argon flowing down of the isobutane by 2-butene] -, and the glass reactor of - porter mold. Subsequently, close [of a catalyst] closes the reactor which is, and then makes it primary reduced pressure, and, subsequently it cools it at the temperature of -15 degrees C.

[0046] Subsequently, isobutane 80.6g is added to the reactor containing a catalyst under stirring. Said reactor is sunk into a -15-degree C cold bath. In order to equalize temperature, a catalyst system + isobutane is left under stirring for 30 minutes.

[0047] In all, 16.5g 2-butene is added regularly and the temperature of a reactor is maintained at -15 degrees C all the time between impregnation time amount for 3 hours.

[0048] A hydrocarbon phase is extracted from a reactor after a reaction, and an isobutane is evaporated slowly. Alkylation objects are collected and this is analyzed by the vapor phase chromatography. The weight composition of this is shown below. The conversion ratio of an olefin is 100 %. The presentation (% of the weight) of an alkylation

object is summarized in the following table 3.

[0049]

[Table 3]

i C ₅	0. 9
C ₆	1. 1
C ₇	1. 3
C ₈	93. 3
C ₉	1. 2
C ₉₊	2. 2

[0050] C8 The research octane number according [a fraction] to count including 93.2% of the weight of a trimethyl pentane is 98.6.

[0051] The contact alkylation test of the isobutane by 2-butene is repeated using the same catalyst as the [example 4] example 3. A series of tests at various temperature are carried out. A result is summarized in the following table 4.

[0052]

[Table 4]

T (°C)	C ₅ - C ₇	C ₈	C ₉₊	R O N
- 2 0	2. 1	95. 2	2. 7	99. 5
- 1 0	4. 0	89. 9	4. 9	97. 3
0	5. 9	87. 8	7. 3	96. 1

[0053] This table clarifies the advantage in the case of operating it at low temperature.

[0054] [Example 5]

Newly in :heptane manufactured [as is the manufacture following of a catalyst / an ion complex with a normality of 0.67 Ns] sublimated 28.8g AlCl₃ 12.9g chloro hydration 4-pico RINIUMU (chlorhydrate de 4-picolinium) is added slowly, stirring with a magnetic stirring rod. Thus, the mixture of a liquid is obtained with a mere ambient temperature colored for a while. This mixture avoids moisture and is saved under an argon.

[0055] Macropore silica 13g of the specific surface area of 27m²/g is activated by baking by 500 ** for bottom 4 hours of air. Thus, the activated solid-state is saved under an argon. Next, it performs desiccation sinking [of 13g of solid-states calcinated by mixture 8.5 g prepared as mentioned above] in. Thus, the acquired catalyst contains mixture 8.5 g and silica 13g, and this is saved under an argon at -18 degrees C.

[0056] The catalyst manufactured according to said approach is introduced into Fischer [of volume 360 ml beforehand purged by alkylation argon flowing down of the isobutane by 2-butene] -, and the glass reactor of - porter mold. Subsequently, close [of a catalyst] closes the reactor which is, and then makes it primary reduced pressure, and, subsequently it cools it at the temperature of -15 degrees C. and the thing carried out in the example 3 by -15 degrees C -- the same -- the contact alkylation test of the isobutane by 2-butene is repeated. A result is summarized in the following table 5.

[0057]

[Table 5]

i C ₅	1 . 1
C ₆	0 . 8
C ₇	1 . 4
C ₈	9 3 . 6
C ₉	1 . 0
C ₉₊	2 . 1

[0058] C8 The research octane number according [a fraction] to count including 94.0% of the weight of a trimethyl pentane is 98.9.

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